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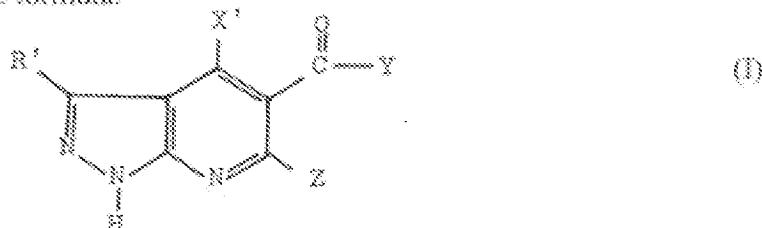
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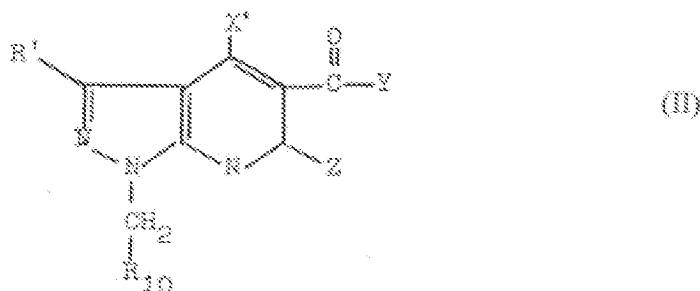
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The present invention relates to a process for the preparation of compounds having the pyrazolo[3,4-b]pyridine nucleus, not being substituted in position 1, that is to say that there is only one free hydrogen and no other substituents on the nitrogen atom in this position, and having various substituents in position 4 and a fixed carbonyl group in position 5. Position 3 may be non-substituted or substituted. Position 6 is preferably, but not necessarily, non-substituted. The substituent in position 4 may be a hydroxy, halogeno, lower alkoxy, acyclic or heterocyclic amino radical of the type described below or a hydrazine group. In position 5, the carbonyl group fixed to the carbon atom in the nucleus may bear a hydroxyl, lower alkoxy, phenyl or substituted phenyl or acyclic or heterocyclic amino group of the type mentioned previously.

The compounds which are prepared by the process according to the invention correspond to the formula:

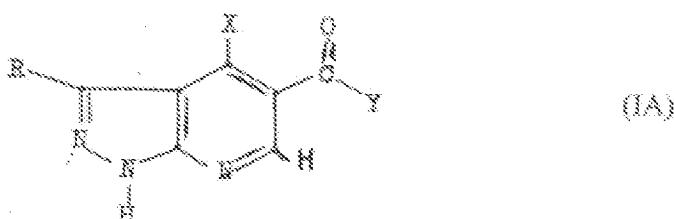


in which R' and Z are each hydrogen or a substituent, X' is a substituent and Z is a substituent; this process is characterised in that a compound with formula:



in which R₁₀ is an aryl or a heterocyclic radical, is oxidised by means of a metallic oxide.

More particularly, pyrazolo[3,4-b]pyridines, which are not substituted in position 1, can be prepared according to this process with a general formula:

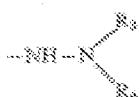


in which R is a hydrogen atom, a phenyl or C₁ to C₇ alkyl group; X is a hydroxy group, a halogeno (preferably chloro) radical, a C₁ to C₇ alkoxy group or acyclic or heterocyclic amino group with formula



where R_1 and R_2 are each a hydrogen atom, a C_1 to C_7 alkyl, a C_1 to C_7 alkenyl, C_1 to C_7 alkanoyl, phenyl, substituted phenyl (for example that the phenyl nucleus contains one or two simple substituents including C_1 to C_7 alkyl, halogeno, trifluoromethyl, amino or carboxy, preferably one of the last three substituents), phenyl-(C_1 to C_7 alkyl), di-(C_1 to C_7 alkyl)-amino- C_1 to C_7 alkyl, or phenyl-(C_1 to C_7 alkanoyl) possibly substituted (where the phenyl group has the aforementioned substituents), for example benzoyl substituted or not. The base group $-NR_1R_2$ may also form a 5- or 6-membered heterocyclic nucleus in which an additional nitrogen atom is present, that is to say pyrrolidine, piperidine, pyrazolyl, pyrimidinyl, pyridazinyl, dihydropyridazinyl or piperazinyl groups. Y is a hydroxyl, C_1 to C_7 alkoxy, phenyl or substituted phenyl group (the substituents of the phenyl group being the same or mentioned previously).

A compound can be obtained in which X is a hydrazine group



in which R_3 and R_4 are each a hydrogen atom, a C_1 to C_7 alkyl or phenyl group, from the previous compound in which X is an alkoxy group or a chloro radical. One can obtain hydrazones from hydrazine, in which R_3 and R_4 are hydrogen atoms by reaction with an aldehyde or a ketone. A compound can be obtained in which Y is an amino group



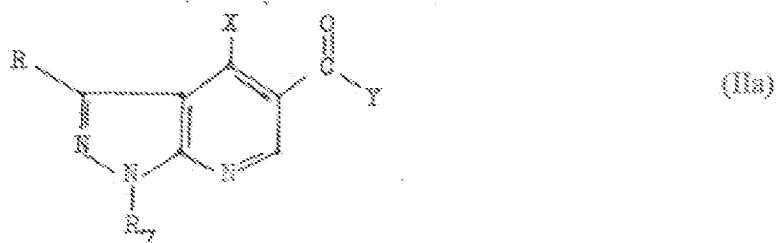
in which R_5 and R_6 have the same significance as R_1 and R_2 , from the previous compound in which Y is an alkoxy group or a chlorine atom.

The C_1 to C_7 alkyl groups in any of the previous groups are straight or branched chain hydrocarbon groups such as methyl, ethyl, propyl, isopropyl, butyl, tert.-butyl, etc. The C_1 to C_7 alkenyl groups are analogue groups having a double bond. The references to the alkoxy groups relate to ether groups bearing alkyl groups of the previous type.

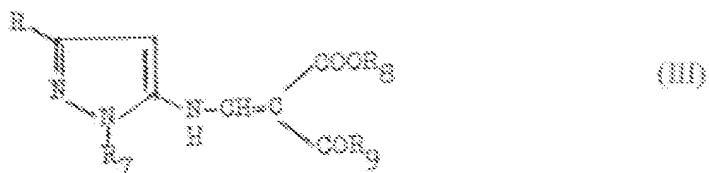
The four halogens are envisaged but chlorine and bromine, especially the former, are preferred.

The lower alkanoyl groups are C_1 to C_7 fatty acid acyl groups.

Pyrazolo[3,4-b]pyridines of the type described above and in particular pyrazolo[3,4-b]pyridines which correspond to formula I, but which have a substituent on the nitrogen atom in position 1, for example those with formula:



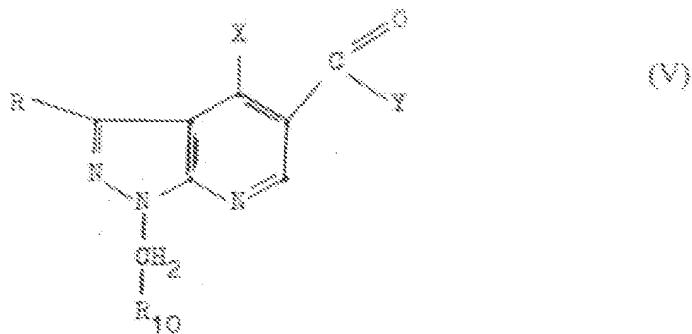
can be prepared directly by cyclisation, or from compounds formed by cyclisation, of 1-substituted-[(*S*-pyrazolyl)amino]-methylene]carboxylic acid esters, for example, compounds with formula:



in which R has the significance above, R₇ is a C₁ to C₇ alkyl, phenyl or phenyl-(C₁ to C₇ alkyl) group, R₈ is a C₁ to C₇ alkyl group and R₉ is a C₁ to C₇ alkoxy, phenyl or substituted phenyl group. This process is not successful for the preparation of 1-non-substituted pyrazolo[3,4-b]pyridines because (pyrazolylamino)-methylene-carboxylic acid esters such as those of formula III in which there is a hydrogen atom on the nitrogen atom instead of group R₇, give, during cyclisation, pyrazolo-pyrimidines with formula:



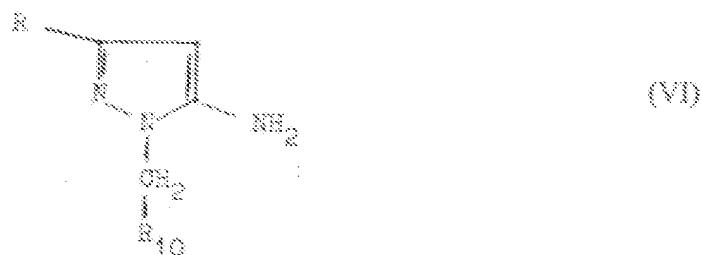
In order to prepare 1-non-substituted pyrazolo[3,4-b]pyridines bearing substituents in positions 4 and 5, namely compounds with formula I, it has now been found that it is necessary to use a 1-arylmethylpyrazolo[3,4-b]pyridine or a 1-heteromethylpyrazolo[3,4-b]pyridine, for example a compound with formula:



in which R, X and Y have the significance above. R₁₀ is a monocyclic or bicyclic carboyclic aromatic nucleus or a 5- or 6-membered heterocyclic nucleus, containing nitrogen, oxygen or sulphur such as phenyl, naphthyl, furyl (which is preferred), thiienyl, pyrrolyl, pyrazolyl, pyridyl, pyrimidyl, pyrazinyl, pyridazinyl, etc. Cyclisation in this way gives the nucleus having the nucleus system desired, and the latter associated with the oxidation stage described below for removing the -CH₂-R₁₀ group gives the desired pyrazolo[3,4-b]pyridine configuration having no substituent in position 1. Variants of groups X and Y can be obtained at certain stages described below.

Compounds with formula II having the arylmethyl or heteromethyl group in position 1, which are oxidised according to the present invention to obtain 1-non-

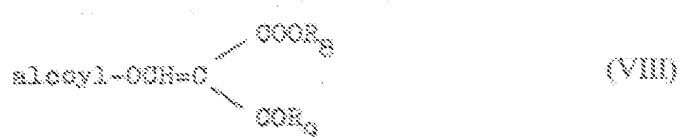
substituted pyrazolo[3,4-b]pyridines, are derived from a 5-aminopyrazole with formula:



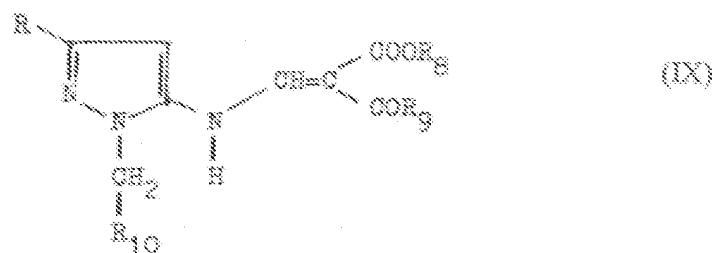
in which R and R₁₀ have the significance above, which can be prepared by the process described in the British patent No. 1057740, by closing the nucleus of an aldehyde hydrazone with formula:



This cyclisation can be carried out by heating at a temperature of about 90° to 130°C, in an inert, liquid, organic solvent, for example an alcohol such as methanol, ethanol, butanol, etc., preferably in the presence of a catalyst such as an alkaline metal alcoholate, for example sodium butylate. This 5-aminopyrazole is made to react with an alkoxy methylene carbonic acid ester with formula:

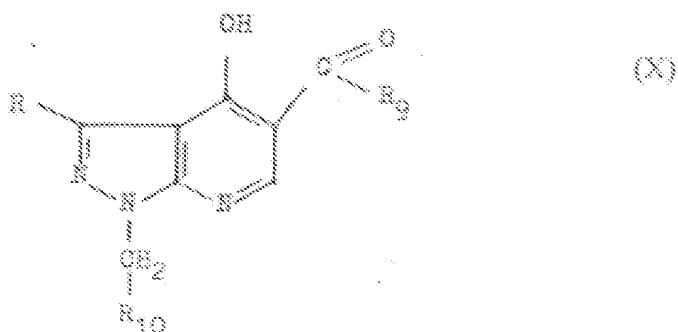


This reaction can be carried out by heating the reagents at a temperature in the region of 120°C for several hours and a compound is obtained with the formula:



Alkoxy methylene carbonic acid esters with formula VIII are known compounds and they can be prepared like ethoxy methylene malonic acid diethyl ester [Organic Syntheses 28, 60-2 (1948)].

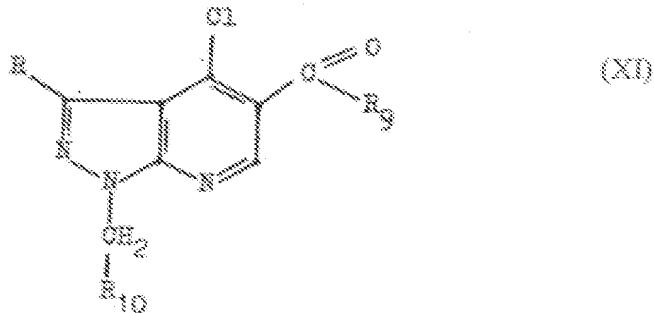
Cyclisation of the compound with formula IX gives a compound with formula:



This cyclisation reaction can be carried out by heating the compound with formula IX in an inert organic solvent such as diphenyl ether, etc., at a temperature of about 230 to 260°C for several hours, whilst the alcohol formed is separated, for example by distillation. The product is then separated from the solvent, for example by fractionated distillation.

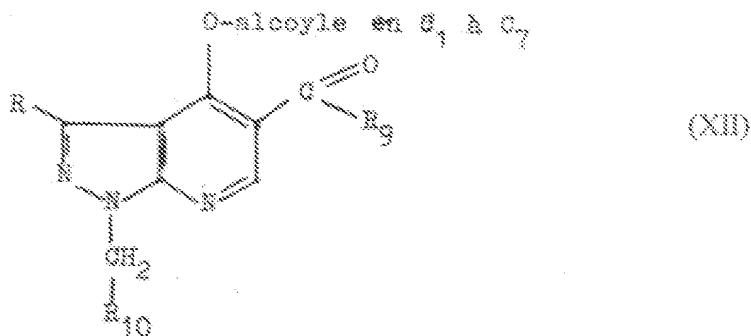
According to a variant, cyclisation of the compound with formula IX can also be carried out by heating it in polyphosphoric acid at a temperature of about 150°C for 5 hours. The product is then separated by dilution with water.

According to another cyclisation process of compounds with formula IX, the product is heated to reflux with phosphorus oxychloride for 15 hours. The excess phosphorus oxychloride is separated by distillation and the compound is separated by treating the residue with iced water. According to this process, the product obtained has the formula:



Instead of cyclising a compound with formula IX with phosphorus oxychloride, according to a variant, a compound with formula XI can be prepared by chlorination of a product with formula X with an inorganic acid chloride such as thionyl chloride or phosphorus oxychloride.

The reaction of a compound with formula X with an appropriate C₁ to C₇ alkyl halogenide in the presence of a metal carbonate such as potassium carbonate gives a compound in which X is a C₁ to C₇ alkoxy group, for example a compound with formula:

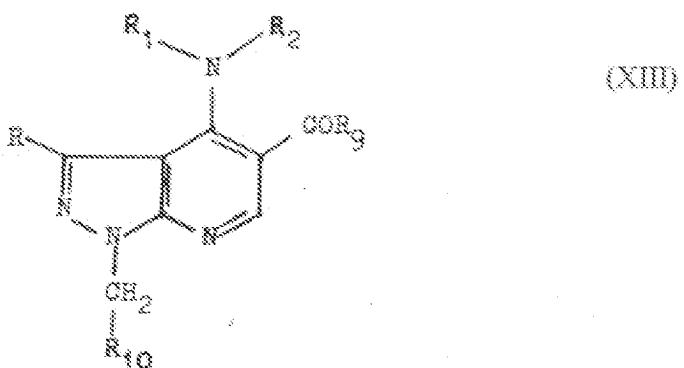


Instead of alkylating, a compound with formula XII can also be synthesised by making a product with formula XI react with a corresponding sodium or potassium alcoholate.

A compound can now be prepared in which X is the amino group



for example a compound with formula:



by making a compound with formula XII or formula XI react with a primary or secondary amine



The pyrazolo[3,4-b]pyridine non-substituted in position 1 according to the present invention is now prepared, by oxidising a compound with formula II, X, XI, XII or XIII with an oxidation agent which is a metallic acid, preferably in an inert organic solvent at a temperature between about 110 and 160°C. One removes the group from the nitrogen atom in position 1, and one obtains a compound with the same formula but having a hydrogen atom on the nitrogen atom in position 1. The oxidation agents which are a metallic oxide include metal oxides such as selenium or chromium at their highest valency, for example selenium dioxide, potassium permanganate, potassium bichromate, chromium anhydride, etc.; selenium dioxide is preferred. Organic solvents for the oxidation reaction include for example diethylene glycol dimethyl ether, acetic acid, etc.

According to a variant, a compound can be obtained in which X is a chloro, lower alkoxy radical or



that is to say, a compound with formula XI and XII and XIII, but having a hydrogen atom in position 1 instead of the $-\text{CH}_2\text{-R}_{10}$ group, by separating the $-\text{CH}_2\text{-R}_{10}$ group of a compound with formula X by the oxidation reaction described above. This compound with formula X, but which is now non-substituted in position 1, is treated with an inorganic acid chloride, such as phosphorus oxychloride or thionyl chloride as described above to obtain a 1-non-substituted-4-chloro compound corresponding to formula XI. This compound with formula XI can now be alkylated with an alkaline metal alcoholate as described above to obtain a 1-non-substituted-4- C_1 to C_7 alkoxy compound with formula XII.

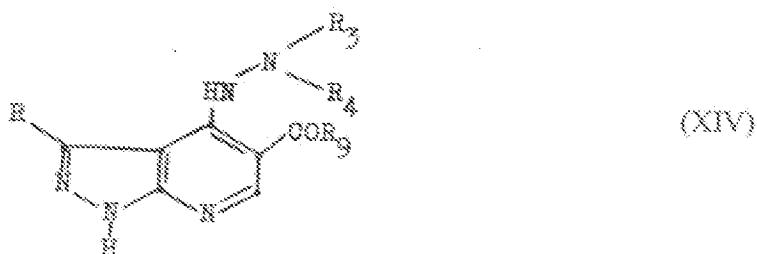
When the 1-non-substituted compound with formula XII is treated with a primary or secondary amine



as described above, a 1-non-substituted-4-amino compound with formula XIII is obtained.

A compound can be prepared in which Y is a hydroxyl group by saponification of the corresponding ester with an alkaline metal hydroxide such as sodium hydroxide.

When a 1-non-substituted pyrazolo[3,4-*b*]pyridine has been obtained having a 4-halogeno radical or a 4- C_1 to C_7 alkoxy group, for example a compound with formula XI or formula XIII, but without the $-\text{CH}_2\text{-R}_{10}$ group, a hydrazine can then be prepared with a formula:

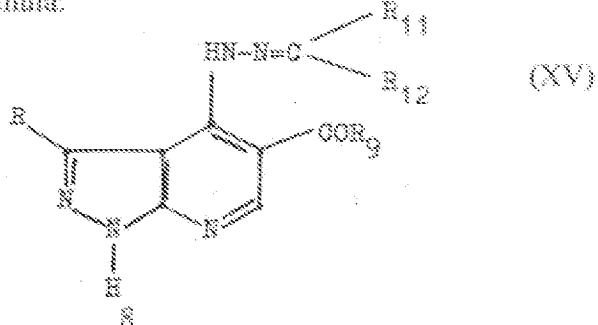


by making a 1-non-substituted compound with formula XI or formula XII react with the appropriate hydrazine in a solvent such as an alcohol. It is sometimes advantageous to use an autoclave.

By the reaction of a compound with formula XIV, in which R_3 and R_4 are both hydrogen atoms, with the appropriate aldehyde or ketone



a compound is obtained with formula:



R_{11} is a hydrogen atom, a C_1 to C_7 alkyl, hydroxy- C_1 to C_7 alkyl, phenyl, substituted phenyl, phenyl- C_1 to C_7 alkyl or (substituted phenyl)- C_1 to C_7 alkyl group; R_{12} is a C_1 to C_7 alkyl, phenyl, hydroxy- C_1 to C_7 alkyl, substituted phenyl, phenyl- C_1 to C_7 alkyl or (substituted phenyl)- C_1 to C_7 alkyl group and R_{11} and R_{12} together are a cyclo-alkyl group. The substituted phenyl groups are the ones mentioned above.

A compound can be prepared with formula IA in which Y is an amino group



by making the corresponding carboxylic acid, that is to say in which Y is a hydroxyl group, react with an inorganic acid chloride, followed by treatment with the appropriate primary or secondary amine.

The various end products obtained by the process according to the invention are useful locally as antimicrobial agents, for example for combating infections due to micro-organisms such as *Staphylococcus aureus*, and also as central nervous system depressant agents for relieving states of anxiety and nervous stress.

The following examples illustrate the invention and preferred embodiments. Other products can be obtained in the same way by changing the ingredients appropriately. All the temperatures are in degrees centigrade.

Example 1:

4-butylamino-3-methyl-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.

A (a) $\{[(1-(2-furyl)methyl-3-methyl-5-pyrazolyl)amino]methylene\}malonic acid diethyl ester.$

177 g (1 mol) of 1-(2-furyl)methyl-3-methyl-5-aminopyrazole and 216 g (1 mol) of ethoxy methylene malonic acid diethyl ester are heated at 130°C until the theoretical quantity of alcohol has been distilled off. The remaining oil, that is to say the $\{[(1-(2-furyl)methyl-3-methyl-5-pyrazolyl)amino]methylene\}malonic acid diethyl ester$ is recrystallised in methanol; 305 g is obtained (88% yield) which melts at 95°C.

(b) *4-hydroxy-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.*

347 g (1 mol) of $\{[(1-(2-furyl)methyl-3-methyl-5-pyrazolyl)amino]methylene\}malonic acid diethyl ester$ is dissolved in 1 litre of diphenyl ether and heated at 240°C for 2 hours. The ethanol formed is continuously distilled off. The solvent is separated under vacuum. The 4-hydroxy-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester remains and it is recrystallised in methanol; 182 g is obtained (60% yield); it melts at 82°C.

(c) 4-ethoxy-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.

150 g (0.5 mol) of 4-hydroxy-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester, 140 g of potassium carbonate and 155 g of ethyl iodide are put into suspension in 500 ml of dimethyl formamide and heated whilst stirring at 60°C for 10 hours. The excess potassium carbonate and precipitated potassium iodide is then filtered. The filtrate is diluted with 500 ml of water. The 4-ethoxy-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester precipitates and is recrystallised in hexane; 125 g is obtained (76% yield); it melts at 82°C.

(d) 4-butylamino-1-(2-furyl)methyl-3-methyl-4-butylaminopyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.

32.8 g (0.1 mol) of 4-ethoxy-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester is dissolved in 190 ml of dioxane and heated to reflux for 5 hours with 11 g (0.15 mol) of n-butylamine. The solvent is then evaporated dry and the residue recrystallised in hexane; 25.5 g (72% yield) of 4-butylamino-1-(2-furyl)methyl-3-methyl-4-butylaminopyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester is obtained which melts at 77°C.

B. 4-butylamino-3-methyl-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.

17.8 g (0.05 mol) of 4-butylamino-1-(2-furyl)methyl-3-methylpyrazolo[3,4-b]pyridine-carboxylic acid ethyl ester and 11.1 g (0.1 mol) of selenium dioxide are put into suspension in 50 ml of diethylene glycol methyl ether and heated at 160°C. A few drops of water are added and the temperature is maintained for 1.5 hours. After cooling, the mixture is filtered and diluted with 20 ml of water. Pale yellow crystals of 4-butylamino-3-methyl-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester are formed and they are recrystallised in ethanol; 10.2 g is obtained (74% yield); it melts at 174-176°C.

Example 2:

4-Butylamino-1H-pyrazolo[3,4-b]pyridine-5-diethylaminocarboxamide.

A (a) [[[1-(4-picoly)-5-pyrazolyl]amino]methylene]malonic acid diethyl ester.

174 g of 1-(4-picoly)-5-aminopyrazole and 216 g of ethoxy methylene malonic acid diethyl ester are heated, whilst stirring, at 140°C until the theoretical quantity of alcohol is distilled off. The reaction mixture crystallises on cooling. After recrystallisation in ethyl acetate 220 g of [[[1-(4-picoly)-5-pyrazolyl]amino]methylene]malonic acid diethyl ester is obtained (65% yield) which melts at 95-97°C.

(b) 4-hydroxy-1-(4-picoly)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester.

86 g (0.25 mol) of [[[1-(4-picoly)-5-pyrazolyl]amino]methylene]malonic acid diethyl ester is heated at 240°C for 15 minutes. The dark oil is cooled and 200 ml of methanol is added. The 4-hydroxy-1-(4-picoly)-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester crystallises freely; 33 g is obtained (44% yield) which melts at 140°C.

B (c) 4-hydroxy-1*H*-pyrazolo-[3,4-*b*]pyridine-5-carboxylic acid ethyl ester.

3 g (0.01 mol) of 4-hydroxy-1-(4-picoly)-1*H*-pyrazolo-[3,4-*b*]pyridine-5-carboxylic acid ethyl ester is dissolved in 20 ml of acetic acid. 2.2 g (0.02 mol) of selenium dioxide and 2-3 drops of water are added. The mixture is heated to reflux for 30 minutes then filtered. 4-hydroxy-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester precipitates on cooling. After recrystallisation in acetic acid 1.8 g is obtained (87% yield); it melts at 275°C.

(d) 4-ethoxy-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester.

4.1 g (0.02 mol) of 4-hydroxy-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester, 5.6 g (0.04 mol) of potassium carbonate and 3.5 g (0.022 mol) of ethyl iodide are heated in 30 ml of dimethyl formamide, whilst stirring, for 10 hours at 60°C. The excess potassium carbonate is then separated by filtration and 30 ml of water is added. The 4-ethoxy-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester precipitates and is recrystallised in methanol; 2 g is obtained (42.5% yield); it melts at 180°C.

(e) 4-butylamino-1*H*-pyrazolo-[3,4-*b*]pyridine-5-carboxylic acid ethyl ester.

2.35 g (0.01 mol) of 4-ethoxy-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester is treated with 2.2 g (0.03 mol) of butylamine at 90°C for one hour. The mixture is then cooled and diluted with 20 ml of water and the white crystalline precipitate is separated by filtration. After recrystallisation in diethyl ether 1.7 g of 4-butylamino-1*H*-pyrazolo-[3,4-*b*]pyridine-5-carboxylic acid ethyl ester is obtained (72% yield) which melts at 181°C.

(f) 4-butylamino-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid.

2.6 g (0.01 mol) of 4-butylamino-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid ethyl ester is treated with 1.1 g of sodium hydroxide in 30 ml of ethanol for 20 hours at normal temperature. The solvent is separated under vacuum and the residue is dissolved in 10 ml of water. After acidification with acetic acid, the 4-butylamino-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid solidifies and is separated by filtration. The product is purified by recrystallisation in acetic acid; 1.9 g is obtained (82% yield); it melts at 225°C.

(g) 4-butylamino-5-diethylaminocarbonyl-1*H*-pyrazolo[3,4-*b*]-pyridine

2.3 g (0.01 mol) of 4-butylamino-1H-pyrazolo[3,4-b]-5-carboxylic acid is heated to reflux with 10 ml of thionyl chloride for 5 hours. The excess thionyl chloride is then separated under vacuum, the residue is dissolved in 20 ml of dry tetrahydrofuran and 2 g of diethylamine added whilst cooling. The mixture is left to stand for 24 hours then the solvent is evaporated dry and 20 ml of water is added to the residue. The 4-butylamino-5-diethylaminocarbonyl-1H-pyrazolo[3,4-b]-pyridine is filtered and recrystallised in ethyl acetate to obtain 2.1 g (70% yield) which melts at 130°C.

Example 3:

4-(2-cyclohexylidene)hydrazino-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.

(a) *4-chloro-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.*

20.7 g (0.1 mol) of 4-hydroxy-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester is heated to reflux for 5 hours with 100 ml of phosphorus oxychloride. The excess phosphorus oxychloride is distilled off and the oily residue is poured onto ice. After neutralisation with aqueous ammonia, the 4-chloro-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester is separated and recrystallised in ethanol; 10.5 g is obtained (47% yield) which melts at 169-171°C.

(b) *4-hydrazino-1H-pyrazolo[3,4-b]-pyridine-5-carboxylic acid ethyl ester.*

5.6 g (0.025 mol) of 4-chloro-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester is dissolved in 10 ml of ethanol and heated to reflux for 15 minutes with 1 ml of hydrazine hydrate. After adding 50 ml of water, the 4-hydrazino-1H-pyrazolo[3,4-b]-pyridine-5-carboxylic acid ethyl ester separates and is recrystallised in butanol; 3.5 g is obtained (64% yield) which melts at 350°C.

(c) *4-(2-cyclohexylidene)hydrazino-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester.*

2.21 g (0.01 mol) of 4-hydrazino-1H-pyrazolo[3,4-b]pyridine-5-carboxylic acid ethyl ester is put into suspension in 5 ml of acetic acid. 1 g of cyclohexanone is added and the mixture is heated to reflux for 10 minutes. 10 ml of water are added. After cooling the 4-(2-cyclohexylidene)hydrazino-1H-pyrazolo[3,4-b]pyridine precipitates and is recrystallised in acetic acid; 2.2 g is obtained (73% yield) which melts at 265°C with decomposition.

Example 4:

5-benzoyl-4-(2-aminobutyl)-1H-pyrazolo[3,4-b]pyridine.

A (a) *[(1-(2-furyl)methyl)pyrazolyl]amino)methylene]benzoyl acetic acid ethyl ester.*

163 g (1 mol) of 1-(2-furyl)methyl-5-aminopyrazole and 248 g (1 mol) of ethoxy methylene benzoyl acetic acid ethyl ester are heated at 130°C until no more alcohol is distilled (approximately 1 hour). The oily residue crystallises and after cooling and recrystallisation in hexane 310 g (85% yield) of [[[1-(2-furyl)methyl-5-pyrazolyl]amino]methylen]benzoyl acetic acid ethyl ester is obtained which melts at 75-77°C.

(b) *5-benzoyl-4-hydroxy-1-(2-furyl)methylpyrazolo[3,4-*b*]pyridine.*

36.5 g of [[[1-(2-furyl)methyl-5-pyrazolyl]amino]methylen]benzoyl acetic acid ethyl ester is dissolved in 50 ml of diphenyl ether and heated to reflux at 260°C for 30 minutes. After distillation of the solvent, a dark oil is obtained which crystallises after adding methanol. After recrystallisation 20 g (61% yield) of 5-benzoyl-4-hydroxy-1-(2-furyl)methylpyrazolo[3,4-*b*]pyridine is obtained which melts at 102°C.

(c) *5-benzoyl-4-ethoxy-1-(2-furyl)methylpyrazolo[3,4-*b*]pyridine.*

3.3 g (0.01 mol) of 5-benzoyl-4-hydroxy-1-(2-furyl)methylpyrazolo[3,4-*b*]pyridine is dissolved in 20 ml of dimethyl formamide, 2.8 g of potassium carbonate and 3.1 g of ethyl iodide are added and the mixture is heated for 12 hours at 60°C. The excess potassium carbonate is filtered and water is added. The 5-benzoyl-4-ethoxy-1-(2-furyl)methylpyrazolo[3,4-*b*]pyridine precipitates and is recrystallised in hexane; 3 g is obtained (86% yield) which melts at 70°C.

B (d) *5-benzoyl-4-ethoxy-1*H*-pyrazolo[3,4-*b*]pyridine.*

1.7 g (0.005 mol) of 5-benzoyl-4-ethoxy-1-(2-furyl)methylpyrazolo[3,4-*b*]pyridine is dissolved in 5 ml of diethylene glycol dimethyl ether; 1.1 g of selenium dioxide is added and the mixture is heated, whilst stirring, at 160°C. After having added a drop of water, the temperature is maintained for one hour. The mixture is filtered under heat and the 5-benzoyl-4-ethoxy-1*H*-pyrazolo[3,4-*b*]pyridine precipitates during cooling. After recrystallisation in butanol 1 g is obtained (77% yield) which melts at 195-197°C.

(e) *5-benzoyl-4-(2-aminobutyl)-1*H*-pyrazolo[3,4-*b*]pyridine.*

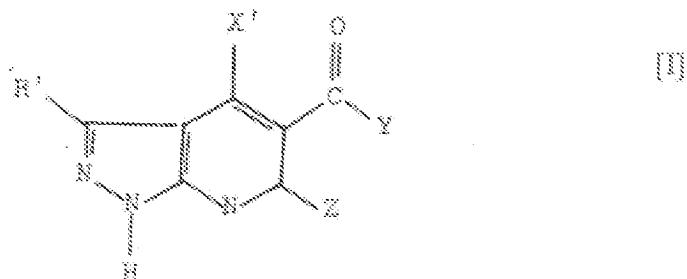
0.65 g (0.0025 mol) of 5-benzoyl-4-ethoxy-1*H*-pyrazolo[3,4-*b*]pyridine is heated to reflux with 1 ml of butylamine for 10 minutes. The mixture is cooled and 10 ml of water is added. 5-benzoyl-4-(2-amino-butyl)-1*H*-pyrazolo[3,4-*b*]pyridine precipitates, it is filtered and recrystallised in butanol; 1.1 g is obtained (76% yield) which melts at 175°C.

By proceeding as in the example shown in the last column, the following compounds with formula IA are prepared:

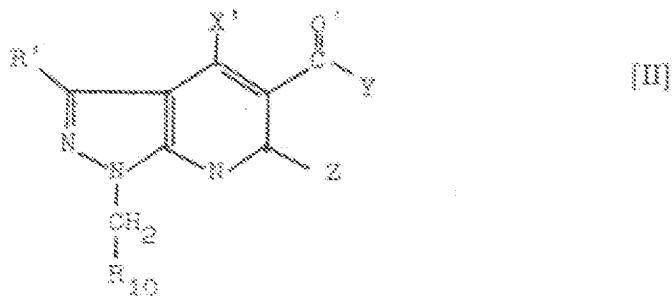
R	X	Y	Melting point °C	Process according to example
H	—OH		300°	4
H	—NH ₂		280°	4
H	HNC ₂ H ₅		212°	4
H ₂ C	HN—C ₂ H ₅	—OH	245-250°	2
H	HN—	—OC ₂ H ₅	224°	1
H ₂ C	—OH	—OC ₂ H ₅	217°	2
H	HNC ₂ H ₅	HN—C ₂ H ₅	227°	2
H	—N—N—	—OC ₂ H ₅	285°	3
H	—N—N—	—OC ₂ H ₅	270°	3

CLAIM

Process for the preparation of a compound with formula



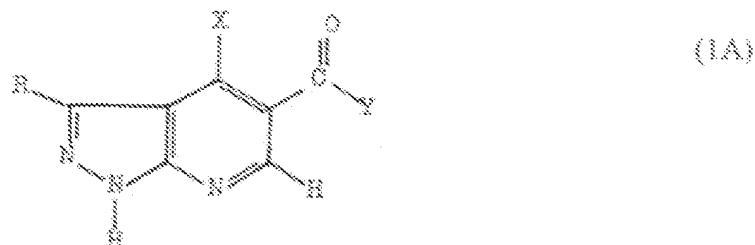
in which R' and Z are each a hydrogen atom or a substituent, X' is a substituent and Y is a substituent, characterised in that a compound with formula



in which R₁₀ is an aryl or heterocyclic radical is oxidised by means of a metallic oxide.

SUB-CLAIMS

1. Process according to the claim, characterised in that the metallic oxide is selenium dioxide.
2. Process according to the claim or subclaim 1, characterised in that, in formulas I and II, X' is a hydroxy, halogeno or C1 to C7 alkoxy substituent.
3. Process according to the claim and subclaim 2, characterised in that, in formula II, R₁₀ is a mono- or bicarboyclic aryl radical.
4. Process according to the claim and subclaim 2, characterised in that, in formula II, R₁₀ is a 5- or 6-membered heterocyclic radical containing one or two nitrogen atoms or a sulphur atom or an oxygen atom.
5. Process according to the claim, characterised in that a compound is prepared with formula

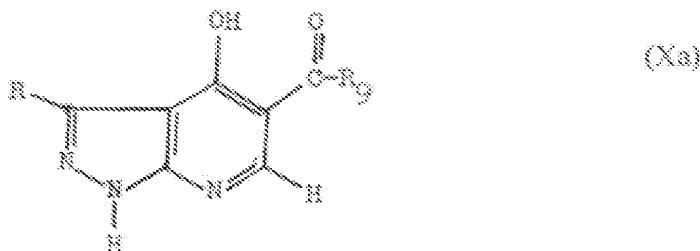


in which: R is a hydrogen atom, a phenyl or C₁ to C₇ alkyl radical; X is a hydroxyl group, a halogen atom, preferably chlorine, a C₁ to C₇ alkoxy group or an amino group with formula

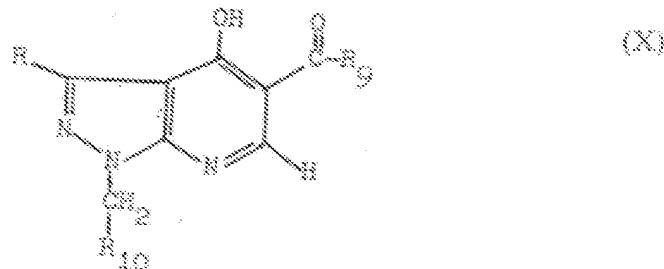


in which R₁ and R₂ are each hydrogen, a C₁ to C₇ alkyl, C₁ to C₇ alkenyl, C₁ to C₇ alkancyl, phenyl possibly substituted, phenyl-(C₁ to C₇ alkyl)-di-(C₁ to C₇ alkyl)-amino-(C₁ to C₇ alkyl)-amino-(C₁ to C₇ alkyl) or phenyl (C₁ to C₇ alkyl) group be substituted [sic]; R₁ and R₂ may also form with the nitrogen atom a 5- or 6-membered heterocycle, and Y is a hydroxy, C₁ to C₇ alkoxy or phenyl possibly substituted group.

6. Process according to the claim and subclaim 5, for the preparation of a compound with formula



in which R has the significance given to subclaim 5 and R₉ is a C₁ to C₇ alkoxy or phenyl possibly substituted group, characterised in that a compound with formula



is heated with selenium dioxide.

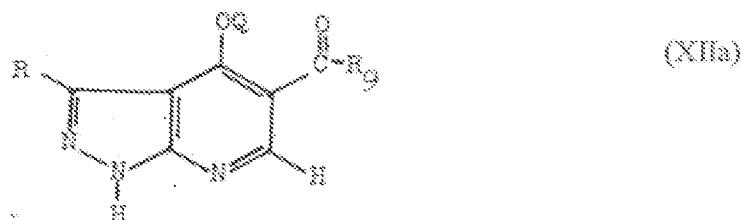
7. Process according to the claim and one of the subclaims 5 and 6, characterised in that, in formulas II and X, R₁₀ is a furyl radical.

8. Process according to the claim and one of the subclaims 5 and 6, characterised in that, in formulas II and X, R_{10} is a pyridyl radical.

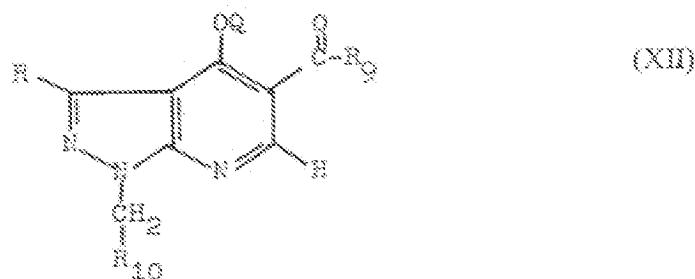
9. Process according to subclaims 6 and 8, characterised in that, in formulas X and Xa, R_9 is a C_1 to C_7 alkoxy radical and R is hydrogen.

10. Process according to subclaim 9, characterised in that R_9 is an ethoxy group.

11. Process according to the claim and subclaim 5, for the preparation of a compound with formula



in which R has the significance given to subclaim 5, R_9 is a C_1 to C_7 alkoxy or phenyl possibly substituted radical, and Q is a C_1 to C_7 alkyl radical, characterised in that a compound with formula



is heated with selenium dioxide.

12. Process according to subclaim 11, characterised in that in formula XII, R is a hydrogen atom and R_{10} is a furyl group.

13. Process according to subclaim 11, characterised in that in formula XII, R is a hydrogen atom, R_{10} is a furyl group and R_9 is a phenyl group.

14. Process according to subclaim 11, characterised in that, in formula XII, R is a hydrogen atom, R_{10} is a furyl group, R_9 is a phenyl group and the C_1 to C_7 alkyl group is an ethyl group.

15. Process according to the claim, characterised in that the $-OH$ group of a compound obtained having this group in position 4 is etherified to prepare a C_1 to C_7 alkyl ether.